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XI. *On a new Variety of Alum.* By JAMES APJOHN, M.D., M.R.I.A.,  
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Read 10th April, 1837.

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THE mineral to which I am about to draw the attention of the Academy was given me by Mr. Smith of College-green, but I have since received a larger specimen of it from W. G. Atherton, Esq., a young gentleman who recently arrived in Dublin from the coast of Africa, for the prosecution of his medical studies, and who informed me that it occurs about midway between Graham's Town and Algoa Bay, in beds of considerable extent, and composed of a number of strata, whose aggregate thickness in some places amounts to at least twenty feet. It closely resembles satin spar, or the finer forms of amianthus. The threads or fibres of which it is composed, and which are very easily separated from each other, are about six inches in length, perfectly transparent, and possessed of a beautiful silky lustre. Upon exposure to air, however, they gradually lose this lustre, and become opaque on the surface, owing to efflorescence. The taste is astringent and sweet, or almost identical with that of common alum. The specific gravity = 1.727, and the aqueous solution reddens litmus, and gives white precipitates, with nitrate of barytes, and caustic potash. These latter properties belong also to common alum. The precipitate, however, afforded by the caustic potash was but partially dissolved by an excess of the alkali, and the residue, though white at first, gradually became brown. A slight examination was sufficient to show that this matter was oxide of manganese, and that the alkali held alumen in solution.

Having thus established the presence in the mineral of sulphuric acid, alumen, and protoxide of manganese, it became highly probable that it was an alum in which the alkali was replaced by oxide of manganese. But before drawing such a

conclusion, it was necessary first to investigate the proportions of the three constituents just mentioned; and, secondly, to determine whether the alkali was or was not altogether absent.

To resolve the latter question, 30.13 grains were dissolved in water, and treated first with ammonia, which threw down the alumen and greater part of the manganese, and then with sulphuretted hydrogen, to complete the precipitation of the latter base. The whole was then thrown upon a filter, and the mixed precipitates being welledulcorated with distilled water, the washings were evaporated to dryness in a porcelain capsule, and then transferred to a counterpoised platinum crucible, in which they were ignited. The residue weighed but .31 of a grain, and upon examination proved to be sulphate of magnesia, with a scarcely appreciable trace of sulphate of lime, in all probability derived from the filter. Hence, as

30.13 : .31 :: 100 : 1.02, the amount of sulphate of magnesia in 100 grains, —and which, as may be easily calculated, includes .71 of a grain of sulphuric acid.

To determine the proportions of acid, alumen, and manganese, 34.47 grains were dissolved in hot water, and nitrate of barytes being added in excess, the precipitate was collected, and well washed with distilled water upon a double filter. Dried at 212° the sulphate of barytes weighed 35.26 grains. Of these 31.13 were exposed to a low red heat, by which they were reduced to 29.71. Hence, as

31.13 : 29.71 :: 35.26 : 33.65, the true weight of the sulphate of barytes. And as

116.8 : 40.1 :: 33.65 : 11.55, the corresponding sulphuric acid. And as

34.47 : 11.55 :: 100 : 33.50, the sulphuric acid in 100 grains of the mineral.

To the washings of the sulphate of barytes, sulphuric acid was added, so as to precipitate the excess of the barytes, and this being separated by a single filter, ammonia was first added in excess, and then a current of sulphuretted hydrogen directed into the solution, by which operations the alumen was thrown down, and the manganese also, partly as oxide, and partly as sulphuret. The mixed precipitate was well washed upon a single filter, and then transferred to a porcelain capsule, where it was digested with caustic potash, with the view of

dissolving the alumina. In the prosecution, however, of the analysis, I became convinced that this method of separation would not answer, for a trace of oxide of manganese was dissolved by the caustic potash, and however great the excess of alkali employed, and however long the digestion, a considerable quantity of alumen remained with the oxide.

To overcome this difficulty, a fresh portion of the mineral (30.4 grs.) was dissolved in water, and precipitated by the yellow ferrocyanide of potassium. The ferrocyanide of manganese thus thrown down, was collected on a single filter, and being well washed, was transferred to a porcelain capsule, in which it was digested with caustic potash. The oxide of manganese thus developed, when collected, washed, and dried, at 212° on a double filter, was found to weigh 4.21 grains. Of these 3.87 were reduced by a white heat to 2.21. Hence, as

$3.87 : 2.21 :: 4.21 : 2.40 =$  red oxide of manganese, or that whose formula is  $Mn_3 O_4$ . And

$38.36 : 35.7 :: 2.4 : 2.23$ , the equivalent quantity of protoxide of manganese. And

$30.4 : 2.23 :: 100 : 7.33$ , the protoxide of manganese in 100 grains of the mineral.

The washings of the ferrocyanide of manganese were now supersaturated with sulphuric acid, and boiled with bicarbonate of soda added in excess, by which the alumen was precipitated. When washed and dried at 212° it weighed 5.89 grs. Of these 5.77 by a red heat were reduced to 3.18. Hence

$5.77 : 3.18 :: 5.89 : 3.24 =$  true weight of alumen.

$30.4 : 3.24 :: 100 : 10.65 =$  alumen in 100 grs. of the mineral.

The following, therefore, are the results of the analysis :—

Sulphuric acid . . . . .	33.50—71 = 32.79
Alumina . . . . .	10.65
Protoxide of manganese . . . . .	7.33
Sulphate of magnesia . . . . .	1.08
Water of crystallization . . . . .	48.15
	100.00

If these numbers be divided by the respective atomic weights, the following will be the quotients :

	(1)	(2)	(3)
For Sulphuric acid . . .	$\frac{32.79}{40.1}$	= .817	4
Alumina . . . . .	$\frac{10.65}{25.7}$	= .414	2.026
Oxide of manganese . .	$\frac{7.33}{35.7}$	= .205	1.003
Water . . . . .	$\frac{48.15}{9}$	= 5.350	26.315

From a comparison of columns (2) and (3) the quotients will be seen to be almost exactly as the numbers 4, 2, 1, and 26, so that the mineral is composed of two atoms of the sesqui-sulphate of alumina, one atom of the sulphate of manganese, and twenty-six atoms of water. Its formula is therefore  $3\text{SO}_3, \text{Al}_2\text{O}_3 + \text{SO}_3, \text{MnO} + 26\text{HO}$ , or exactly conformable to that which belongs to soda alum.

It is well known that the neutral sulphate which enters as a proximate constituent into the composition of alum is not necessarily always the same. Chemists are long acquainted with the fact, that this sulphate may be one of potash, ammonia, or soda. More recently also it has been shown, that the alumina might be replaced indifferently by the sesqui-oxides of iron, chrome, and manganese, without disturbing the formula, or even the crystalline form of the salt, which in every instance is an octohedron. The species, however, whose examination has been just concluded, differs from all these in not containing any alkali, the place of this being occupied by the protoxide of manganese, and in not crystallizing in the octohedral form. I have attempted to crystallize it by evaporation in the presence of oil of vitriol in vacuo, but could only obtain a mass of a fibrous structure, closely resembling the mineral in its original state. I have also attempted unsuccessfully the synthetic production of this alum, by mixing sesqui-sulphate of alumina and sulphate of manganese in the proper proportions; the solution concentrated by evaporation, and then placed beneath the receiver of the air-pump with the oil of vitriol, could not be brought at all to the solid state. As this failure may be owing to the employment of too great an excess of sulphuric acid, I purpose repeating the experiment with all the necessary precautions, and with the addition of the one per cent. of sulphate of magnesia detected in the native product. This latter, indeed, can scarcely be considered as an essential component, as it in all probability merely replaces some sulphate

of manganese ; magnesia, and protoxide of manganese, being isomorphous substances. This hypothesis, it must be admitted, does not receive any support from the analytic results, as there is no deficiency of manganese ; but the amount of the sulphate of magnesia is very small, and the discrepancy in question may well be due to errors of experiment.

As the alkali of alum may be replaced by the protoxide of manganese, and since, as Mitscherlich has shown, the alumina may be replaced by sesqui-oxide of manganese, it is obviously theoretically possible that an alum should exist containing no metal but manganese. I have not as yet had time to bring this anticipation to the test of experiment.

I shall conclude with one or two remarks, naturally suggested here, upon the important doctrines of isomorphism, first promulgated by Professor Mitscherlich of Berlin. These doctrines are generally considered as supported and well illustrated by the constitution and form of the different kinds of alum. This, however, would appear to be only partially true. Alumina, peroxide of iron, and the sesquioxides of manganese and chrome, having a similar composition, and being supposed (the two first certainly are so) isomorphous, we can understand how they might replace each other in alum without affecting its crystalline form. This is quite intelligible, and squares with the doctrines of Mitscherlich. But soda may, we know, be substituted for potash and ammonia, with neither of which it is isomorphous, and the octohedral form still subsist. Moreover, ammonia, potash, and soda alums contain—the two first twenty-four, the last twenty-six atoms of water, and nevertheless the crystal of each is a regular octohedron. These facts do not appear to be in accordance with the laws of isomorphism, as far as these have been hitherto developed, but I am far from thinking that they do not admit of explanation. The latter difficulty, for example, may be removed by supposing that the different varieties of alum have, as Professor Graham supposes, in reality the same quantity of combined water, and attributing the different proportions given by experiment to inevitable errors of manipulation, or to water mechanically interposed between the plates of the crystals.

In conclusion, I may observe, that upon the principles under consideration, the alum which I have described ought not to crystallize as an octohedron, inasmuch as the protoxide of manganese is not isomorphous with the alkalies.